

# **Report as of FY2007 for 2007ND149B: "Iron Nanoparticles for the Treatment of the Herbicides Atrazine, Alachlor and Dicamba in Groundwater"**

## **Publications**

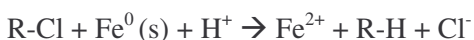
- Conference Proceedings:
  - ◆ Thompson, Jay M., Achintya N. Bezbaruah, Bret J. Chisholm, 2007, Rapid Dechlorination of the Herbicide Alachlor by Zero Valent Iron Nanoparticles. ISNEPP 2007, Nanotechnology in Environmental Protection and Pollution, 11-13 December. Ft. Lauderdale, FL (Presentation)
  - ◆ Thompson, Jay M., Achintya N. Bezbaruah, Bret J. Chisholm, 2007, Iron Nanoparticles for the Treatment of the Herbicides Atrazine, Alachlor and Dicamba in Groundwater. 2 nd International Conference on Environment, 2-5 August. Athens, Greece (Presentation)
  - ◆ Thompson, Jay M., Achintya N. Bezbaruah, Bret J. Chisholm, 2007, Laboratory Scale Study to Determine the Effectiveness of Iron Nanoparticles for Selected Pesticide Remediation. 2007 AWRA Summer Specialty Conference, Emerging Contaminants of Concern in the Environment: Issues, Investigations, and Solutions, 25-27 June. Vail, CO (Poster)

## **Report Follows**

# Iron Nanoparticles for the Treatment of the Herbicides Atrazine, Alachlor and Dicamba in Groundwater

## Introduction/Background on Research Topic

Iron metal has been used for the remediation of contaminated groundwater for about two decades [20]. The most common mode of contaminant degradation by iron is reductive dehalogenation, which can be explained by the relationship below [20, 35].



Typically, iron for remediation is in the form of filings or microscale powder. In this manner, iron has been used in the field and laboratory to remediate water contaminated with chlorinated ethanes [11, 22], chlorinated methanes [20], arsenic [19], and pesticides [5, 8, 14, 26, 28]. The advantages of iron metal for remediation include its non-toxicity, economy, and faster reaction rates than biological processes. The above reaction has been shown to be surface area dependant [35]. Because of the relatively low surface area of iron filings and powder, reactions may be slow or incomplete, resulting in possibly toxic degradation by-products [11].

With the development of nanoscale zero-valent iron (nZVI) for environmental remediation, many of the problems associated with iron filings were resolved [37]. Iron nanoparticles are typically 1-100 nm in diameter. This results in specific surface areas on the order of 20-30 m<sup>2</sup>/g [18, 23] compared to about 0.05 and 5 m<sup>2</sup>/g for iron filings and lab-grade iron micropowder, respectively [11, 36].

Research has shown that nZVI can successfully degrade chlorinated ethenes [34], chlorinated methanes [17], PCBs [34], arsenic [13], and other metals [23] in anoxic environments. Additionally, a recent study has shown that some pesticides can be treated by nZVI in oxic conditions [12]. Advantages of nZVI over microparticles include improved economics of direct injection into the aquifer, very fast reaction rates and more complete reactions.

Pesticides, including herbicides, insecticides and fungicides, are among the many contaminants successfully treated by conventional iron powder or iron filings. Numerous studies have demonstrated success on the bench scale and field scale. Research has shown that pesticides, when applied and handled properly, will not accumulate to high levels in groundwater [16]. However, accidents and spills can and do happen, often resulting in very high pesticide concentrations [2]. Iron nanoparticles have shown potential to remediate such spills.

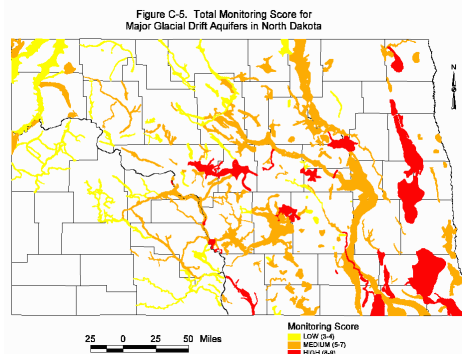
While the proposed nZVI/pesticide trials have been largely successful in the laboratory (see “*Research Progress Made*”), the final goal of the work proposed in the 2007 NDWRRI program was a small-scale pesticide spill remediation technology. To achieve this, a delivery vehicle is needed. Polymeric delivery vehicles have been developed that both disperse nZVI and protect it from non-target species [27]. Unfortunately, these polymeric coatings are synthetic and thus, may not be desirable in the subsurface. While this may be an acceptable trade-off for highly toxic and recalcitrant chlorinated solvent sites, this is an unsuitable approach for smaller, less toxic pesticide spills.

For the proposed application, the delivery vehicle must be biodegradable, economic and relatively simple to use. Calcium alginate is an ideal candidate for this application. This work aims to entrap and encapsulate (two distinct technologies) nZVI in calcium alginate with the end goal being a product that can be easily emplaced in a trench or bore hole for site remediation. Alginate entrapment/encapsulation is a process where nZVI is captured in an alginate matrix (entrapment) or encapsulated in a thin-walled alginate capsule (encapsulation). Although the entrapped/encapsulated nZVI (E/E nZVI) will lack many of the specialized properties of more advanced polymeric vehicles, it will be biodegradable, inexpensive, and simple to emplace.

### Description of the Critical State or Regional Water Problem to be Investigated

Clean, safe groundwater for drinking is critical for North Dakota. Sixty percent of North Dakota's population use groundwater as their drinking water source [24]. In rural areas, where pesticide contamination is more likely to occur, 97% of the population depends on groundwater [45]. Protection of this resource is of vital interest to the people of North Dakota.

Modern agricultural practice has prevented high-level non-point source contamination of ground water [16]. While vigilance must be maintained on non-point source contamination, a more immediate problem is the point source contamination of groundwater at agricultural chemical retail outlets and pesticide storage, mixing, and loading facilities on farms. North Dakota water quality officials cite the release of the herbicides used to control leafy spurge, such as dicamba, at these retail outlets [3]. In Minnesota, the most common pesticide contamination scenario is the accidental release of corn herbicides at agricultural chemical retail outlets [33]. The North Dakota Department of Health has conducted a study on the vulnerability of groundwater to pesticide contamination. The results are summarized in **Figure 1**. Note that the vulnerable aquifers of the southeast coincide with the state's highest concentration of corn acreage and thus chloroacetanilide consumption [10]. Although this work is focused on state environmental issues, pesticide contamination is national [15, 32] and even global [30] concern.



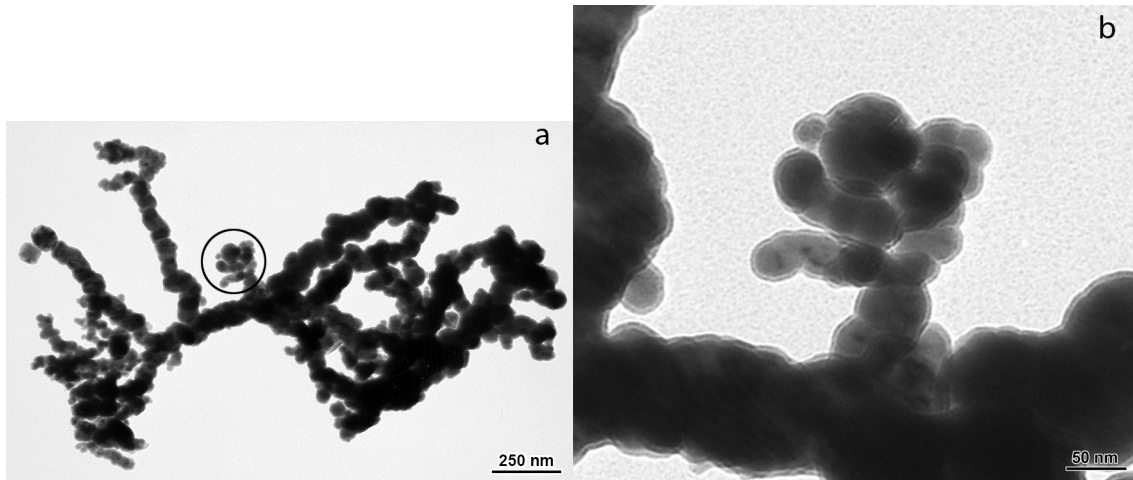
**Figure 1:** Aquifers in North Dakota Vulnerable to Pesticide Contamination. [24]

### Research Progress Made

A short progress summary is provided below. Please note that the new work proposed for the 2008 program has begun as well.

#### *nZVI Synthesis and Characterization*

Particles were successfully synthesized in the manner proposed in the 2007 submission. Particles were characterized by transmission electron microscopy, X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) surface area analysis. Average particle diameter and specific surface area were determined to be 35 nm and 25 m<sup>2</sup> g<sup>-1</sup>, respectively. Typical nZVI morphology is presented in **Figure 2**.



**Figure 2 (a):** Transmission electron microscopy image of an nZVI cluster. **(b)** Expanded image of area indicated in **(a)**.

#### *Degradation Batch Trials*

As proposed, atrazine and alachlor degradation trials were conducted. Atrazine degradation was found not to occur in the presence of nZVI. A variety of buffer and acid injection conditions were attempted to facilitate dechlorination, however, none yielded atrazine degradation. While further acid injection would likely allow nZVI mediated reduction [7], such a system would not have practical applications. Thus, atrazine trials were concluded.

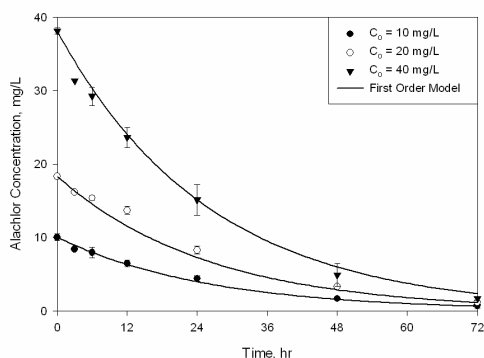
Alachlor (2-Chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide) degradation trials using nZVI were conducted as proposed. Alachlor dechlorination proceeded rapidly and was complete. First order kinetics adequately described the nZVI mediated degradation of alachlor ( $R^2 = 0.999$ ). The following pseudo first order rate equation was proposed:

$$\frac{dC}{dt} = k_{SA} \rho_A C$$

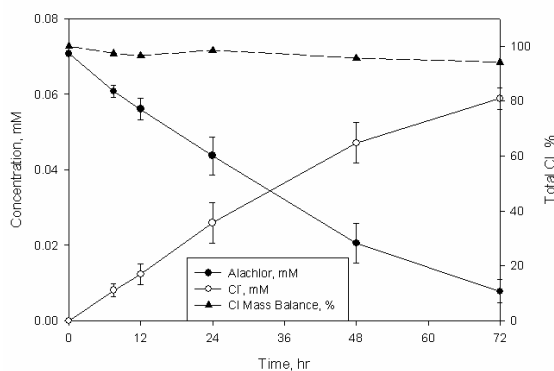
where  $C$  is alachlor concentration ( $\text{mg L}^{-1}$ ),  $k_{SA}$  is the surface area normalized rate constant ( $38.5 \times 10^{-5} \text{ L m}^{-2} \text{ hr}^{-1}$ ) and  $\rho_A$  is the iron surface area concentration ( $\text{m}^2 \text{ L}^{-1}$ ). Experimental and modeling results are presented in **Figure 3**.

The degradation byproduct of the above reaction was determined by GC-MS to be dechlorinated alachlor (N-(2,6-Diethylphenyl)-N-(methoxymethyl)acetamide). This finding was confirmed by the stoichiometric transfer of chlorine from alachlor to chloride ions as the reaction progressed (**Figure 4**). Although the toxicology and persistence of this compound are unknown, the dechlorinated species of metoachlor, a structurally similar herbicide, was found to be roughly five times more biodegradable than its parent compound [6, 31]. Thus, it is likely that the byproduct of the observed reaction is a more environmentally benign compound than its parent.

A comparison of microscale and nanoscale zero valent iron for alachlor degradation was also conducted. As expected, nZVI mediated reactions progressed more quickly than microscale iron on a mass normalized basis. Perhaps less expectedly, nZVI performed 5-10 times better than microscale iron a surface area normalized basis. It is assumed that the higher ratio of active to inactive surface area in nZVI accounted for this difference. One goal of the mechanistic studies proposed in this document is to better elucidate this phenomenon.



**Figure 3:** Alachlor degradation and modeling results in the presence of nZVI at differing initial concentrations. Iron mass loading:  $4 \text{ g L}^{-1}$ . Error bars represent  $\pm$  standard error. Controls (not shown) do not display appreciable alachlor degradation.



**Figure 4:**  $\text{Cl}^-$  evolution during alachlor degradation. Iron mass loading:  $4 \text{ g L}^{-1}$ . Error bars represent  $\pm$  standard error. Dotted line represents the percentage of Cl (alachlor +  $\text{Cl}^-$ ) recovered in IC and HPLC analyses.

The research will be useful for the development of an nZVI permeable reactive barrier with improved hydraulic characteristics. This is significant because research on practical, inexpensive applications of nZVI is scarce. Furthermore, the proposed (and completed) research may have applications in the development of an inexpensive on-site pesticide waste treatment system. Such a system could potentially treat low-volume, high-concentration pesticide wastewater and rinsewater much more economically than the centralized treatment system used presently.